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Summary

In order to simplify the analysis of malathion, ethanolic potassium hydroxide solution was adopted for hydrolysis of malathion in carbon tetrachloride solution. This improved method was applied in determining malathion residues in the rice plant and the chinese chabbage.

For the extraction of the residues, methanol was used as a solvent. In the residue determination of the chinese cabbage extracts, clean-up by chromatography on acid-washed alumina was efficient to isolate malathion. The proposed analytical method is able to determine as small as about 0.25 ppm of malathion contained in plant materials.

Some field tests were undertaken to determine malathion residues sprayed on rice plants and chinese cabbges. When 0.025% malathion emulsion was applied to rice plants in autumn, 1.4 ppm of malathion was remained in the rice plants after 6 days. It shows that more than 90% of malathion deposited was disappeared within 6 days. When 0.05% malathion was applied to chinese cabbages in winter, 7.4 ppm was remained after 6 days. More than 75% was disappeared.

To estimate half-life value and effective period to insects, regression equations were calculated by log log 10×ppm malathion residues and days elapsed after applications. The half-life values calculated were smaller than those by Gunther-Blinn's method. From the slope of the equations, the disappearance of malathion on and in plants is faster under higher temperature.

Systemic Insecticidal Properties of Certain Organic Phosphorus Compounds to the Green Peach Aphid, *Myzus persicae* Sulzer, and the Tobacco Cutworm, *Prodenia litura* Fab. Tetsuo Saito and Hachiro Honda (Laboratory of Applied Entomology, Faculty of Agriculture, Nagoya University, Anjo, Aichi, Japan.) Received February 11, 1966. *Botyu-Kagaku* 31, 77. 1966

11. モモアカアブラムシおよびハスモンヨトウに対する有機燐化合物の浸透殺虫力について

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現存の浸透殺虫剤は吸収性口器を有する害虫には有効であるが，咀しやく性口器を有する害虫には効果が低い．咀しやく性口器を有する害虫に有効な浸透殺虫剤を探索するためにモモアカアブラムシおよびハスモンヨトウをもちいて各種有機燐化合物のカンラン苗における浸透殺虫力をしらべた．

現存の浸透殺虫剤および大部分の供試化合物はハスモンヨトウよりもアブラムシに有効であったが，Comp. No. 2662, *O, O*-dimethyl dichlorohydroxyethyl phosphonate, その acetyl 化合物，dipterex およびその ethyl methyl 体はアブラムシよりもハスモンヨトウに強い浸透殺虫力を示した．

Introduction

Systemic action has long been recognized as a desirable character in insecticides, and many efforts have been done to find such insecticides. The first practically useful toxicants of this general class have been certain compounds of selenium (Hurd-Karrer and Poos 1936). The high toxicity of selenium compounds to mammals prevented their use for food crops. They were used against only insects on florist crops in a greenhouse. The next major development in this field was discovery of two systemic organophosphates, dimefox and schradan, and their systemic activity was demonstrated by Schrader and Kukenthal in 1941 (Geary 1953).

Since recent development of insect control by chemicals, many compounds with systemic properties are now known. However, all current systemics still have certain shortcomings.

They are ineffective against chewing insects and some of them have a high level of mammalian toxicity, and are phytotoxic in certain types of applications.

This paper reports screening tests of organophosphorus compounds as systemic insecticides. The object of present experiments was to find out compounds having systemic activity against chewing insects.

Materials and Methods

Adult of the green peach aphid, *Myzus persicae* Sulzer, was employed as an representative of sucking insects and the third instar larvae of the tobacco cutworm, *Prodenia litura* Fab., was an representative of chewing insects. Aphids were collected from cabbage cultured in a greenhouse. The tobacco cutworms, Kōzu strain, were reared for successive generations on sweet potato leaves and potato tubers at 25°C. 75 R.H.

Cabbage plants of the variety Nagaoka Kōhai Shikitori were seeded in a seed bed and transplanted three times, and young plants with five or six leaves were employed as the test plants.

Organophosphorus compounds to be tested were refined more than 90 per cent purities, supplied by Nihon Kagaku Kogyo Co. and Sankyo Co. The test compounds were formulated with acetone : benzene : emulsifier (Newcol-863), 30 : 30 : 30% W/W. One gram of this formulated concentrate was added to 99 m*l* of Kasugai's water culture solution (pH 6-7) and mixed thoroughly to give complete emulsification.

Each test plant was cultured with 100 m*l* water culture solution in a brownish glass pot for 24 hours at 25°C. under fluorescent light. Then ten aphids or five worms were placed in a cupper screened aphid chamber respectively. The chambers were fixed on the third and forth leaves of the test plants. The mortality was observed after 24 hours. Each experiment was replicated twice. All the candidate compounds which showed insecticidal activity at the concentration of 1,000 ppm were submitted further tests at lower concentrations.

Results and Discussions

Results of systemic tests of the established systemic insecticides are shown in table 1. It is apparent that these compounds were highly toxic to the aphid but they were less toxic to the worm, and there is no direct correlation between both insect intoxicities.

Table 1. Systemic insecticidal activity of some systemic insecticides to the green peach aphid, *Myzus persicae* L., and to the tobacco cutworm, *Prodenia litura* Fab.

Insecticide	Mortality			
	Aphid		Worm	
	1,000 ppm	100 ppm	1,000	100
Thiol methyl demeton	100%	90	60	0
Thiono methyl demeton	100	95	60	10
Thiol ethyl demeton	100	85	70	0
Thiono ethyl demeton	100	100	30	0
Phorate	100	50	20	0
Disyston	80	85	40	0
Schradan	90	70	0	0
Check		(0)		(0)

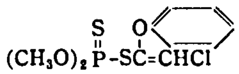
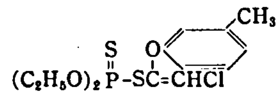
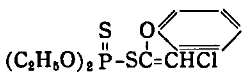
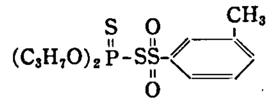
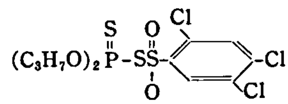
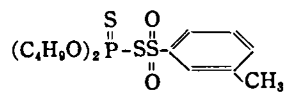
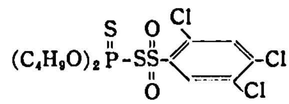
Data from the first systemic experiments with the thiophosphate series are presented in table 2. All the candidates appeared in the same sequence as for table 1 except comp. no. 1961-1 which was only effective to the worm.

Results of the systemic activities for phosphate series are shown in table 3. Five of the candidates, comp. no. 2520, 2522, 2523, 2525 and 2527, were highly toxic to the worm as well as the aphid.

Table 4 shows systemic insecticidal activities of phosphonate series to both insects. The most active compound among this series are dipterex, comp. no. 2651, 2662, 2664 and 2666. These compounds were submitted further test with the both insects to evaluate systemic activity at lower concentration in comparing with schradan (table 5).

Schradan was effective to the aphid but not effective to the worm, while some of new phosphonate compounds, comp. no. 2662, *O*, *O*-dimethyl

Table 2. Systemic insecticidal activity of some thiophosphate esters to the green peach aphid and to the tobacco cutworm at 1,000 ppm.

Comp. No.	Chemical structure	Mortality Aphid	Mortality Worm	Comp. No.	Chemical structure	Mortality Aphid	Mortality Worm
2726		45%	0	2766		60%	0
2731		65	0	3133		65	0
2747	$(CH_3O)_2\overset{S}{\overset{\|}{P}}-S\overset{OC_2H_5}{\overset{\mid}{C}}=CCl_2$	70	0	3134		70	0
2748	$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}-S\overset{OCH_3}{\overset{\mid}{C}}=CCl_2$	55	0	3135		60	0
2750	$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}-S\overset{OC_2H_4OCH_3}{\overset{\mid}{C}}=CCl_2$	60	0	3136		75	0
2751	$(CH_3O)_2\overset{S}{\overset{\|}{P}}-S\overset{OC_4H_9}{\overset{\mid}{C}}=CCl_2$	40	0	4603	$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}-SCH_2COOC_2H_5$	50	0
2754	$(CH_3O)_2\overset{S}{\overset{\|}{P}}-S\overset{OCH_3}{\overset{\mid}{C}}=CCl_2$	70	0	4720	$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}-SCH_2SCH_2F$	80	0
2756	$(CH_3O)_2\overset{S}{\overset{\|}{P}}-S\overset{OC_3H_7}{\overset{\mid}{C}}=CCl_2$	55	0	1961-1	$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}-SCH_2COOC_2H_4Cl$	0	50
2757	$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}-S\overset{OC_3H_7}{\overset{\mid}{C}}=CCl_2$	60	0	1961-2	$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}-SCH_2SCH_2SC_2H_5$	30	10
2765	$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}-S\overset{OCH_3}{\overset{\mid}{C}}BrCCl_2Br$	60	20	1115	$(C_3H_7O)_2\overset{S}{\overset{\|}{P}}-O-\overset{S}{\overset{\|}{P}}(OC_3H_7)_2$	60	20

dichlorohydroxyethyl phosphonate and its acetyl compounds, comp. no. 2664, and dipterex, *O, O*-dimethyl trichlorohydroxyethyl phsphonate, and its ethyl methyl homologue of comp. no 2666 were more toxic to the worm than the aphid.

David and Gardiner (1954) have applied demeton to roots of plants and found that it showed insecticidal activities on larvae of *Phaedon cochleariae* F. and *Pieris brasicae* L. but the dose which killed *phaedon* larvae was, about twice and that of *Fieris* larvae was 20 to 200 times as much as that of aphid. Many sucking insects are well controlled by systemic insecticides and a good deal of the liturature has been collected and reviwed by Ripper in 1957.

Johansen (1956) studied comparisons of structural changes and insecticidal activity by systemic action with several series of thiophosphates. He noted that an increase in the length of the chain beyond two carbon atoms on either side of the sulfur linkage reduced the systemic insecticidal activity of the esters.

Also, clark *et al* (1955) pointed out that maximum systemic activity against the two spotted spider mite was obtained when R was ethyl in the compound having general formula of $(RO)_2P(S)SCH_2SR'$, which was synthesized from *O, O*-dialkyl hydrogen phosphorodithioate with formalin and mercaptan.

In decreasing order of toxicity was : methyl, isopropyl, and *n*-propyl. Considering R', highest activity was obatined when it is ethyl or isopropyl. Increasing the chain length decreases the activity, and no further activity in R=dodecyl.

Table 3. Systemic insecticidal activity of some phosphate esters to the green peach aphid and to the tobacco cutworm at 1,000 ppm.

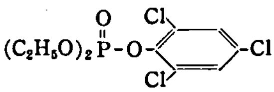
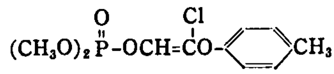
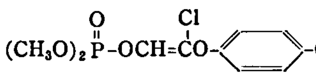
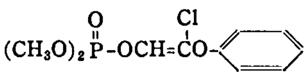
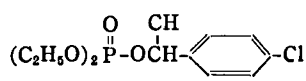
Comp. No.	Chemical structure	Mortality Aphid	Mortality Worm	Comp. No.	Chemical structure	Mortality Aphid	Mortality Worm
1114		50%	0	2528		30%	30
2502	$(C_2H_5O)_2P(O)\text{-}OCH{=}C(Cl)SC_2H_5$	65	10	2529	$(C_3H_7O)_2P(O)\text{-}OCH(Cl)C(Cl)NO$	95	10
2512		55	60	2531	$(CH_3O)_2P(O)\text{-}OCH(Br)C(Br)(Cl)OC_4H_9$	25	0
2520		85	90	2532	$(CH_3O)_2P(O)\text{-}OCH{=}C(Cl)OC_2H_4OC_2H_5$	45	0
2522	$(CH_3O)_2P(O)\text{-}OCH(Cl)CCl_3$	100	80	2533	$(CH_3O)_2P(O)\text{-}OCH{=}C(Cl)OC_2H_4OC_4H_9$	100	0
2523	$(CH_3O)_2P(O)\text{-}OCH(Br)C(Br)Cl_2$	50	90	2534	$(ClCH_2CH_2O)_2P(O)\text{-}OCH{=}CHCl$	65	30
2525	$(CH_3O)_2P(O)\text{-}OCH(Cl)C(NO_2)Cl_2$	100	80	1961-3	$(C_2H_5O)_2P(O)\text{-}OCH(CN)CH_3$	10	0
2526	$(C_2H_5O)_2P(O)\text{-}OCH(Cl)C(NO_2)Cl_2$	75	20	1961-8	$(C_2H_5O)_2P(O)\text{-}OC(O{=}P(OC_2H_5)_2){=}CCl_2$	0	10
2527	$(C_2H_5O)_2P(O)\text{-}OCH(Cl)CCl_3$	80	80	1961-9		0	10

Table 4. Systemic insecticidal activity of some phosphonate esters to the green peach aphid and to the tobacco cutworm at 1,000 ppm.

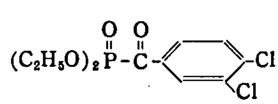
Comp. No.	Chemical structure	Mortality Aphid	Mortality Worm	Comp. No.	Chemical structure	Mortality Aphid	Mortality Worm
Dipterex	$(CH_3O)_2P(O)\text{-}CH(OH)CCl_3$	90%	100	2666	$(CH_3O)(C_2H_5O)P(O)\text{-}CH(OH)CCl_3$	75%	90
1104	$(C_2H_5O)_2P(O)\text{-}CCl_3$	15	0	2667	$(CH_3O)(C_2H_5O)P(O)\text{-}CH(OCOCH_3)CCl_3$	15	40
2612	$(C_2H_5O)_2P(O)\text{-}COCCl_3$	20	0	1961-5	$(C_2H_5O)_2P(O)\text{-}CH(CCl)CH_2NO_2$	10	30
2651	$(CH_3O)_2P(O)\text{-}CH(OCOCH_3)CCl_3$	55	90	1961-6	$(C_2H_5O)_2P(O)\text{-}CCl_2CH{=}CH_2NO_2$	0	20
2662	$(CH_3O)_2P(O)\text{-}CH(OH)CHCl_2$	95	100	1961-10		0	40
2664	$(CH_3O)_2P(O)\text{-}CH(OCOCH_3)CHCl_2$	60	90				

Table 5. Systemic insecticidal activity of some organophosphorus esters to the green peach aphid and to the tobacco cutworm at various concentrations.

Comp. No.	Mortality						Comp. No.	Mortality					
	Aphid			Worm				Aphid			Worm		
	100ppm	10	1	100	10	1		100ppm	10	1	100	10	1
Schradan	70%	15	0	0	0	0	2527	0%	—	—	30	—	—
Dipterex	25	0	0	100	30	0	2651	5	—	—	50	—	—
2520	0	—	—	40	—	—	2662	15	0	0	100	20	0
2522	10	—	—	30	—	—	2664	5	0	0	90	20	0
2523	10	0	0	60	30	0	2666	25	0	0	100	30	10
2525	0	—	—	0	—	—							

Their findings are obviously in accordance with the results obtained for comp. no. 4603, 4720, 1961-1 and 1961-2 and 2726, 2731, 2756 and 2757 in table 2.

Arthur and Casida (1957) studied on metabolism and selectivity of dipterex and its acetyl and vinyl derivatives, they observed that the vinyl phosphate, DDVP, was generally more toxic but less selectively toxic than the other two phosphonates. The low mammalian toxicity of dipterex appears to be due to phosphonate hydrolysis by serum esterase and the elimination of trichloro-portion of the molecule in the urine as trichloroethyl glucronide. And they observed that the systemic activity of dipterex and its vinyl derivative was higher than that of acetyl derivative against pea aphid, but there was difference in selective toxicities by systemic action in different species of insects.

An interesting point is that some of the phosphonate compounds were more effective against the worm than the aphid. A number of investigators have attempted to show mechanism of selective toxicity of systemic insecticides (O'Brien 1961). Further experiments will be held to elucidate on the mechanism of selective toxicity of these compounds.

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Summary

The systemic insecticidal activities of several phosphorothiorates, phosphates and phosphonates were examined against the tobacco cutworm and the green peach aphid. Some phosphonates were more effective to the worm than the aphid, although established systemic insecticides and many tested compounds were only effective to the aphid.

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